

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

PCT

To:

see form PCT/ISA/220

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY
(PCT Rule 43*bis*.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.
PCT/GB2007/050189

International filing date (day/month/year)
10.04.2007

Priority date (day/month/year)
13.04.2006

International Patent Classification (IPC) or both national classification and IPC
INV. C07C51/14 C07C67/38 C07F15/00

Applicant
LUCITE INTERNATIONAL UK LIMITED

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☒ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☒ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

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see form
PCT/ISA/210

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**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/GB2007/050189

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:

- ☒ the international application in the language in which it was filed
- ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).

2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application and necessary to the claimed invention, this opinion has been established on the basis of:

a. type of material:

- ☐ a sequence listing
- ☐ table(s) related to the sequence listing

b. format of material:

- ☐ on paper
- ☐ in electronic form

c. time of filing/furnishing:

- ☐ contained in the international application as filed.
- ☐ filed together with the international application in electronic form.
- ☐ furnished subsequently to this Authority for the purposes of search.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

4. Additional comments:

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/GB2007/050189

Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been examined in respect of

- ☐ the entire international application
- ☒ claims Nos. 1-9,11-13 (all partially)

because:

- ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international search (*specify*):
- ☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):
- ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed (*specify*):
- ☒ no international search report has been established for the whole application or for said claims Nos. 1-9,11-13 (all partially)
- ☐ a meaningful opinion could not be formed without the sequence listing; the applicant did not, within the prescribed time limit:
 - ☐ furnish a sequence listing on paper complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.
 - ☐ furnish a sequence listing in electronic form complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.
 - ☐ pay the required late furnishing fee for the furnishing of a sequence listing in response to an invitation under Rules 13~~ter~~.1(a) or (b).
- ☐ a meaningful opinion could not be formed without the tables related to the sequence listings; the applicant did not, within the prescribed time limit, furnish such tables in electronic form complying with the technical requirements provided for in Annex C-*bis* of the Administrative Instructions, and such tables were not available to the International Searching Authority in a form and manner acceptable to it.
- ☐ the tables related to the nucleotide and/or amino acid sequence listing, if in electronic form only, do not comply with the technical requirements provided for in Annex C-*bis* of the Administrative Instructions.
- ☒ See Supplemental Box for further details

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/GB2007/050189

Box No. V Reasoned statement under Rule 43b/s.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	=
	No: Claims	<u>1-13</u>
Inventive step (IS)	Yes: Claims	=
	No: Claims	<u>1-13</u>
Industrial applicability (IA)	Yes: Claims	<u>1-13</u>
	No: Claims	=

2. Citations and explanations

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

8/27/2009
The prior art as cited in the International Search Report:

- D1: BELLABARBA R M ET AL: "Synthesis, X-ray characterisation and reactions of a trigonal planar palladium(0) carbonyl complex, (tbp_x)PdCO" CHEMICAL COMMUNICATIONS, no. 15, 7 August 2003, pages 1916-1917
- D2: CLEGG W ET AL: "Synthesis and reactivity of palladium hydrido-solvento complexes, including a key intermediate in the catalytic methoxycarbonylation of ethene to methylpropanoate" JOURNAL OF THE CHEMICAL SOCIETY, DALTON TRANSACTIONS, no. 17, 7 September 2002, pages 3300-8
- D3: CLEGG W ET AL: "Characterisation and dynamics of [Pd(L-L)H(sol_v)]⁺, [Pd(L-L)(CH₂CH₃)]⁺ and [Pd(L-L)(C(O)Et)(THF)]⁺ (L-L = 1,2-(CH₂PBu^t)₂C₆H₄): key intermediates in the catalytic methoxycarbonylation of ethene to methylpropanoate" ORGANOMETALLICS, vol. 21, no. 9, 29 April 2002, pages 1832-1840
- D4: EDELBACH B L ET AL: "Catalytic hydrogenolysis of biphenylene with platinum, palladium, and nickelphosphine complexes" ORGANOMETALLICS, vol. 17, no. 22, 1998, pages 4784-4794
- D5: KIM B-G ET AL: "Synthesis and theoretical study of palladium (II) complexes with aminophosphines as 7-membered chelate rings" BULLETIN OF THE KOREAN CHEMICAL SOCIETY, vol. 18, no. 11, 1997, pages 1162-1166
- D6: REDDY N P ET AL: "Unexpected cross-metathesis between Si-C and Si-Si bonds" CHEMICAL COMMUNICATIONS, no. 16, 1996, pages 1865-1866
- D7: JP 08 134218 A (AGENCY IND SCIENCE TECHN) 28 May 1996
- D8: UCHIMARU Y ET AL: "Ring-opening polymerisation of 1,1,2,2-tetramethyl-1,2-disilacyclopentane via palladium complex-catalysed Si-Si bond metathesis" CHEMISTRY LETTERS, no. 2, 1995, page 164
- D9: PORTNOY M ET AL: "Reactions of Electron-Rich Arylpalladium Complexes with Olefins. Origin of the Chelate Effect in Vinylation Catalysis" ORGANOMETALLICS, vol. 13, no. 9, 1994, pages 3465-3479
- D10: WURST K ET AL: "Synthesis and structure of the platinum (0) compounds [(dipb)Pt]₂(COD) and (dipb)₃Pt₂ and of the cluster Hg₆[Pt(dipb)]₄ (dipb = (i-Pr)₂P(CH₂)₄P(i-Pr)₂)" ZEITSCHRIFT FÜR ANORGANISCHE UND ALLGEMEINE CHEMIE, vol. 395, 1991, pages 239-250
- D11: TANAKA M ET AL: "Synthesis of ketones via carbonylation of organic halides. II. Palladium-catalysed carbonylation of organic halides with terminal acetylenes in the presence of amines. Novel acetylenic ketone synthesis" NIPPON KAGAKU KAISHI, no. 3, 1985, pages 537-546
- D12: MOLANDER G A ET AL: "Synthesis and application of chiral cyclopropane-based ligands in palladium-catalyzed allylic alkylation" JOURNAL OF ORGANIC CHEMISTRY, vol. 69, no. 23, 12 November 2004, pages 8062-8069
- D13: BRAUER D J ET AL: "Reactions of coordinated ligands. XIV. Synthesis of a tetradentate phosphorus macrocycle in a palladium (II) template" CHEMISCHE BERICHTE, vol. 119, no. 1, 1986, pages 349-365
- D14: DIAS A R ET AL: "Synthesis and characterization of .eta.5-monocyclopentadienyl (p-nitrobenzonitrile)ruthenium(II) salts: second harmonic generation powder efficiencies" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 475, no. 1-2, 26 July 1994, pages 241-245

Re Item III.

The subject-matter of claim 1 is very broad in its formulation such that there are numerous anticipations of its subject-matter. Taking the subject-matter of the 4 examples (far too few considering the scope of the claims!) as a starting point we have investigated compounds having a central group 8-10 metal atom having chelated thereto a bidentate bisphosphine ligand where the phosphines together with the central metal atoms are part of a 7 membered ring, the other members of the ring being 4 adjacent carbon atoms. With X being halide we have found numerous anticipations (323 in the registry file of CA to be exact falling under this particular generic scope, a large proportion of which we could cite as novelty destroying), too many to list in the International Search Report. The other possibilities for X as given in claim 1 were also investigated. The search is therefore only to be considered complete for claim 10 as a result.

Re Item V.

Novelty

As already indicated above under Item III, even restriction of the subject-matter of the application to compounds having a central group 8-10 metal atom having chelated thereto a bidentate bisphosphine ligand where the phosphines together with the central metal atoms are part of a 7 membered ring, the other members of the ring being 4 adjacent carbon atoms, yielded various compounds falling under the presently-claimed scope for the case that X was halide. As examples of these compounds we can cite:

dichloropalladium (1,2-bis-(di-tert-butylphosphinomethyl)benzene) - disclosed in D1-D3 (novelty-destroying to claims 1-4, 8-10).

diiodopalladium (1,2-bis-(di-tert-butylphosphinomethyl)benzene) - disclosed in D2 (novelty-destroying to claims 1-4, 8-10).

dibromopalladium (1,2-bis-(di-tert-butylphosphinomethyl)benzene) - disclosed in D2 (novelty-destroying to claims 1-4, 8-10).

dichloropalladium (1,4-bis-(diethylphosphino)butane) - disclosed in D4.

dichloropalladium (1,4-bis-(dimethylphosphino)butane) - disclosed in D5. D5 also discloses further Pd compounds which fall under the scope of claims 1-4, 8-10.

dichloropalladium (1,4-bis-(di-n-butylphosphino)butane) - disclosed in D6, D7, D8 and D11 (novelty-destroying to claims 1-4, 8, 9). All the dichloropalladium species listed in Table 1 of D11 are to be seen as novelty-destroying, some also to claim 10. D11 would also appear novelty-destroying to the subject-matter of claims 6 and 13 (see abstract).

dichloropalladium (1,4-bis-(diisopropylphosphino)butane) - disclosed in D9 (novelty-destroying to claims 1-4, 8, 9).

dichloroplatinum (1,4-bis-(diisopropylphosphino)butane) - disclosed in D10 (novelty-destroying to claims 1-4, 8, 9).

dibromonickel (1,2-bis-(diphenylphosphonomethyl)cyclopropane) - disclosed in D12 (novelty-destroying to claims 1-4).

A number of compounds disclosed in D13 - although tetradentate ligands, these compounds fall under the more general scope of claim 1. In the paragraph bridging pages 362 and 363 a hydrogencarbonate salt is prepared. (Novelty-destroying to claims 1, 2, 5, 8, 9).

Finally, in D14, the 3rd (nitrate) species in Table 1 on page 242 is also seen to fall under the presently-claimed scope (novelty-destroying to claims 1-5, 8, 9).

Referring to the prior art patent literature cited in the opening paragraphs of the application, it would appear that the presently-claimed subject-matter is novel.

Concerning the claims relating to the preparation of the compounds of claim 1, although the restricted search did not come up with any documents actually falling under the scope of these claims, the subject-matter of these claims would appear so trivial that it cannot be excluded that there is prior art falling under the scope of these claims for compounds

falling outside the searched scope.

Inventive step

Document D11 would appear the most interesting document for inventive step as the complexes disclosed therein already have been used for the same purpose as claimed in claims 6 and 11. Compared with the disclosures of the patents cited as prior art in the opening paragraphs of the description, it would appear that the only difference over these disclosures lies in the X substituent in the compounds of claim 1 as the ligand portion of the metal complexes is to be seen as well known from these prior art disclosures. As the present set of claims is clearly not novel and as the International Search Authority has no idea how the applicant is going to restrict the subject-matter of the claims to overcome the pending objections, a further investigation of inventive step is not possible at this stage of the proceedings. If the applicant opts for Chapter II proceedings, he should file an amended set of claims and take position on inventive step over the documents cited, especially D11 and the patent documents cited in the description. Concerning the fact that the description only exemplifies 4 compounds, the International Search Authority is of the opinion that a possible inventive step has not been shown to be present (i.e. the invention has not been credibly shown to work) over a broad scope.

Re Item VII.

The application should mention the disclosures of documents D1-D14 briefly (Rule 5.1(a)(ii) PCT). Of the patent documents cited in the opening paragraphs of the application, the second one cited (page 1, line 17) would appear erroneous - EP-A-04489472. We have noticed that EP-A-0489472 is mentioned 2 lines later.

Re Item VIII.

Claim 4 refers to formulae (I)-(V). The claims should not rely on reference to the description but should be self contained. Formulae (I)-(V) should therefore be incorporated into the claims.

**WRITTEN OPINION OF THE
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AUTHORITY (SEPARATE SHEET)**

International application No.

PCT/GB2007/050189